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PB-298 471

# Effects of Suspended Sediments on Photolysis Rates of Dissolved Pollutants

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**TECHNICAL REPORT DATA**
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| 1. REPORT NO. | 2. | 3. |
|---|---|---|
| EPA-600/J-79-013 | JOURNAL ARTICLE | PB 298471 |

| 4. TITLE AND SUBTITLE | 5. REPORT DATE |
|---|---|
| Effects of Suspended Sediments on Photolysis Rates of Dissolved Pollutants | 6. PERFORMING ORGANIZATION CODE |

| 7. AUTHOR(S) | 8. PERFORMING ORGANIZATION REPORT NO. |
|---|---|
| Glenn C. Miller and Richard G. Zepp | |

| 9. PERFORMING ORGANIZATION NAME AND ADDRESS | 10. PROGRAM ELEMENT NO. |
|---|---|
| Environmental Research Laboratory<br>U. S. Environmental Protection Agency<br>College Station Road<br>Athens, GA 30605 | 1HE775<br>11. CONTRACT/GRANT NO. |

| 12. SPONSORING AGENCY NAME AND ADDRESS | 13. TYPE OF REPORT AND PERIOD COVERED |
|---|---|
| U.S. Environmental Protection Agency--Athens, GA<br>Environmental Research Laboratory<br>College Station Road<br>Athens, GA 30605 | Journal Article<br>14. SPONSORING AGENCY CODE<br>EPA/600/01 |

15. SUPPLEMENTARY NOTES

Published in Water Research 13(5):453 to 459, 1979.
Contact: R. G. Zepp, 8-250-3428.

16. ABSTRACT

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17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|
| Photolysis, Mathematical models | Aquatic systems<br>Natural waters<br>Solar photolysis<br>Sediment | 07D<br>07E<br>18B<br>06F<br>13B<br>68D |

| 18. DISTRIBUTION STATEMENT | 19. SECURITY CLASS (This Report) | 21. NO. OF PAGES |
|---|---|---|
| Release to public | Unclassified | 9 |
| | 20. SECURITY CLASS (This page) | 22. PRICE |
| | Unclassified | A02-A01 |

EPA Form 2220-1 (9-73)

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SPRINGFIELD, VA. 22161

EPA-600/J-79-013
JOURNAL ARTICLE
0043-1354/79/0501-0453$02.00/0

*Water Research* Vol. 13, pp. 453 to 459
Pergamon Press Ltd 1979. Printed in Great Britain.

# EFFECTS OF SUSPENDED SEDIMENTS ON PHOTOLYSIS RATES OF DISSOLVED POLLUTANTS

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(*Received* 27 *July* 1978; *received for publication* 24 *November* 1978)

**Abstract**—Data are presented concerning the effects of suspended sediments upon photolysis rates of dissolved ultraviolet (u.v.) absorbing pollutants. The malachite green leucocyanide actinometer was found to be a convenient and sensitive device for measurement of solar u.v. radiation (~330 nm) in sediment suspensions. Irradiance measurements by the actinometer were employed to compute diffuse attenuation coefficients for sediment suspensions from six natural water bodies in Georgia, Mississippi, and Montana. Specific attenuation coefficients were remarkably similar for all the sediments examined. Evidence is presented that large underestimates of photolysis rates result when beam attenuation coefficients of turbid water bodies are employed to compute the effects of light attenuation. Finally, it is demonstrated that photolysis rates within the photic zone are generally more rapid in turbid than in clear water. Enhanced photolysis rates in turbid waters are attributed to the increased diffuseness of light caused by scattering.

## INTRODUCTION

Laboratory evaluations of the photochemical degradation of pollutants in water have generally centered on direct photochemical reactions in distilled water. A quantitative understanding of the fate of a pollutant in a natural water body, however, requires consideration of indigenous materials in the water. Suspended sediments represent one important class of such materials.

Procedures described by Zepp & Cline (1977) are successful in predicting direct photolysis rates of pollutants in pure water and in waters containing dissolved u.v.-absorbing materials. The present studies were designed to extend the utility of this approach to water bodies containing suspended sediments. "Suspended sediments" collectively refer to the clays, silts, and sands that constitute the largest fraction of suspended matter in many rivers and lakes.

The main objectives of this investigation were: (1) to obtain quantitative data on the effects of suspended sediments on the penetration of solar ultraviolet radiation into natural waters; (2) to determine the influence of light scattering on photolysis rates of u.v.-absorbing chemicals in sediment suspensions; and (3) to assess the magnitude of the error that results when beam attenuation coefficients of turbid water bodies are employed to compute the effects of light attenuation on photolysis rates of aquatic pollutants. Ultraviolet light was the focus of these studies primarily because many pollutants absorb sunlight most strongly in this wavelength region.

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## EXPERIMENTAL

### *Materials*

Suspensions of river and pond sediments were obtained either by taking water containing the sediment directly from the source or by resuspending bottom sediment in tap water (Table 1). Because stable suspensions were required for the experiments, each sediment suspension was allowed to settle for 24 h. The supernatant that was used was taken from the top 10 cm of the sample. Thus, it contained particles with diameters less than approximately 2 $\mu$m (defined by Stokes Law) (Jackson, 1956).

Malachite green leucocyanide (MGLC) was synthesized from malachite green (Pfaltz & Bauer) by the procedure of Calvert & Rechen (1952) except for the following differences. The initial precipitate of MGLC was dissolved in 1% HCl and stirred for 1 h. Saturated trisodium phosphate solution was then added until precipitation was complete (pH 6). (Care must be taken with this step—addition of too much phosphate results in formation of malachite green carbinol, which considerably complicates the purification of MGLC.) The resulting precipitate was again collected and dissolved in ethyl acetate. The organic layer was washed with acidified water (pH 5) until no blue coloration was apparent. Then it was evaporated and the MGLC was recrystallized three times from 1:1 methanol–ethyl acetate containing 0.5% acetic acid [m.p. 181.5°–182.5°C (Fisher Johns Apparatus); lit m.p. 176°–177°C (Calvert & Rechen, 1952)]. Use of a safe light was not necessary because the MGLC did not react under standard fluorescent lighting.

Hectorite No. 34 from Hector, California; Halloysite No. 12 from Bedford, Indiana; and Kaolinite No. 4 from Macon, Georgia, were obtained from Ward Scientific Company. Commercial humic acid (Fluka AG) was obtained from Columbia Organic Chemical Co.

$\gamma$-Methoxy-*m*-trifluoromethylbutyrophenone (I) was synthesized by the procedure of Wagner *et al.* (1972), then purified by column chromatography and vacuum distillation (b.p. 86°–87°C, 1 mm) mass spectrum: no parent, m/e 188, 173, 145, 59 (base), 45; NMR $\delta$ 1.9 (*m*, 2H), 2.9 (*t*, 2H), 3.2 (*s*, 3H), 3.4 (*t*, 2H), 7.3–8.2 (*m*, 4H).

Only spectroquality solvents were used.

Table 1. Suspended sediment sources and organic contents

| Sediment | Source | Organic carbon content (%) |
|---|---|---|
| Oconee River* | Athens, Georgia | 1.42 |
| USDA Pond* | Watkinsville, Georgia | 1.61 |
| Hickory Hill Pond† | Watkinsville, Georgia | 1.99 |
| Broad River* | Watson's Mill State Park, Georgia | 1.38 |
| Missouri River† | Northeastern Montana | 0.91 |
| Mississippi River† | Northwestern Mississippi | 1.47 |

* The suspended sediment was obtained directly from the water body.
† Bottom sediments were resuspended in tap water.

*Equipment*

Analyses of the reaction mixtures containing (I) was performed on a Tracor MT-220 gas chromatograph equipped with $^{63}$Ni electron capture detector and a 2 m in length × 2 mm i.d. column containing 1.95% OV-210–1.5% OV-17 on 80/100 Gas Chrom Q. Ultraviolet spectra were obtained on a Perkin–Elmer Model 356 spectrophotometer. Analyses of the MGLC actinometer solutions were performed on a Perkin–Elmer Model 602 digital spectrophotometer.

*Procedures*

The total concentration of suspended and dissolved solids in a sediment suspension was determined by evaporating a known volume of the suspension to dryness in a tared flask and reweighing. The dissolved salt contribution was obtained by centrifuging a portion of the suspension at 16,000 rev/min$^{-1}$ (Sorval Ultracentrifuge) for 1 h and evaporating a known volume of supernatant in a tared flask. The concentration of dissolved salts was then subtracted from the concentration of total solids to compute the concentration of suspended sediments. Ultraviolet absorption spectra of the supernatants were obtained.

Organic carbon content of the sediments was determined by Galbraith Laboratories.

Solar u.v. irradiance in sediment suspensions was measured using actinomer solutions of MGLC $2.0 \times 10^{-3}$ M in 95% ethanol containing $10^{-3}$ M HCl (Fisher *et al.*, 1967)] contained in 10-ml, ground-glass-stoppered round bottom flasks made of Pyrex. Because of various problems associated with working directly in the streams and ponds containing the suspended sediments, a metal tub (62 cm in diameter; 28 cm deep) was used to contain the waters. The inner sides were painted black to minimize back reflection. After filling the tub with the sediment suspensions, the round-bottom flasks were transported to the bottom of the tub in amber bottles to shield against u.v. light. The flasks were then inverted and suspended from clamps on ringstands in the center of the tub such that shading from the ringstand was minimized. Refraction of sunlight at the water surface caused radiation even from angles near the horizon to be bent down sufficiently that direct shading from the sides was eliminated. Exposure times ranged from 15 sec to 10 min, depending on the turbidity of the suspensions, time of day, and time of year. The exposures were adjusted so that the absorbance (1.00 cm pathlength) of the malachite green dye at 622 nm was between 0.25 and 0.8. To compensate for the diminution of light intensity with increasing depth, the flasks at greater depths were usually exposed longer than those near the surface. When the attenuation coefficient was computed for a pair of readings, the absorbance values of the actinometers were corrected for this time differential. The round-bottom flasks were assumed to be spherical collectors and were shown to intercept light identically from all directions except at the neck of the flasks.

Suspensions of the clays, hectorite, halloysite and kaolinite, were allowed to settle for 24 h. The stock clay suspensions were obtained by decanting the top 10 cm of the 20-cm deep suspensions. Dilutions of the stock suspensions were made to give the desired concentrations. Clay suspensions (200 ml) containing various concentrations of clay and $4.2 \times 10^{-6}$ M (I) were simultaneously exposed to midday sunlight in 10 × 5 cm Pyrex dishes at a depth of 2.9 cm. Samples (2.00 ml), taken at appropriate time intervals, were extracted by isooctane and the organic layer was analyzed for (I) by gas chromatograph. Total time of each experiment was 90 min. Rate constants were obtained employing the integrated first-order rate expression using a least-squares analysis of data.

Photolysis rate constants for (I) ($4 \times 10^{-6}$ M) dissolved in sediment suspensions were obtained as described in the preceding paragraph with the exceptions that crystallizing dishes (9.8 × 18.4 cm) were the containers and the suspensions were 8.4–9.7 cm deep. The sides of the crystallizing dishes were covered with aluminum foil and the bottoms with black tape. Photolysis rate constants were also determined for solutions of (I) in distilled water that were exposed to sunlight at the same time as the suspensions. In all cases, no degradation of (I) occurred in dark controls.

## RESULTS AND DISCUSSION

Quantitative descriptions of the transmission of solar radiation in natural waters have been presented by Tyler & Preisendorfer (1962) and Smith & Tyler (1976). The transmittance of light passing through a column of water can be described either in terms of a beam attenuation coefficient, $\alpha$, or a diffuse attenuation coefficient, $K$. The distinction between these terms is important when considering natural waters. Beam transmittance ($T$) refers to the transmittance of a collimated beam of light:

$$T = e^{-\alpha l}, \quad (1)$$

where $\alpha$ is the total beam attentuation coefficient and $l$ is the pathlength. Light attenuation in a natural water results from two independent mechanisms, scattering and absorption, and $\alpha$ equals the sum of the absorption coefficient, $a$, and the total scattering coefficient, $s$.

$$\alpha = a + s. \quad (2)$$

Scattering refers to a directional change of photons out of the beam, and absorption denotes any process whereby the photons are changed into some other form of energy. The scattering coefficient may be further subdivided into forward and back scattering components, $s_f$ and $s_b$, respectively. Diffuse attenuation coefficients $K$ are derived from direct measurements of solar irradiance $I(z)$ at various depths in a water body, equation (3). The terms $I(z)$ and $K$ are wavelength-dependent.

$$K = -\frac{1}{I(z)}\frac{\mathrm{d}I(z)}{\mathrm{d}z}. \quad (3)$$

Several approximate but useful relationships between beam and diffuse attenuation coefficients, equations (4 and 5), have been derived (Smith & Tyler, 1976).

$$\alpha \simeq K + s_f, \quad (4)$$

$$K \simeq Da + s_b. \quad (5)$$

The distribution function, $D$, is related to the radiance distribution and ranges from a minimum of 1 for collimated radiation to a maximum of 2 for completely diffuse radiation. Because solar middle u.v. radiation is derived mainly from the sky (Leighton, 1961), the values of $D$ and $K$ in this spectral region are almost independent of solar altitude (Smith & Baker, 1979).

For a non-homogeneous medium such as a sediment suspension, the beam attenuation coefficient measured in a conventional spectrophotometer is usually greater than the diffuse attentuation coefficient directly measured in the medium under sunlight. The primary reason for this difference is the influence of forward scattering, which removes light flux from the beam. Solar radiance measured in a water body includes both the forward scattered light as well as the light that has not been absorbed. The diffuse attenuation coefficient, therefore, provides the best measure of light penetration into a sediment-laden water body.

*Diffuse attenuation coefficients*

Diffuse attenuation coefficients were computed from solar irradiance measurements in suspensions of natural sediments obtained from several water bodies in the United States (Table 1). The malachite green leucocyanide actinometer (Fisher *et al.*, 1967) was found to be a convenient and sensitive device for measurement of solar irradiance in the middle u.v. region. Upon exposure to u.v. light, MGLC photoionizes to form the highly colored dye, malachite green, the absorption maximum of which is at 622 nm. As long as conversion of MGLC to malachite green is kept low, the buildup in absorption at 622 nm is directly proportional to the number of photons absorbed. The spectral response curve of the MGLC actinometer and near-surface solar spectral irradiance (Zepp & Cline, 1977) were used to compute the wavelength dependence of the photolysis rate of the actinometer (Fig. 1). The average wavelength of sunlight absorption is near 330 nm in both summer and winter.

Experiments were conducted by suspending small, spherical, Pyrex flasks containing MGLC solution in a large container that was filled with sediment suspension and fully exposed to sunlight. Coefficients in Table 2 were computed by equation (6):

$$K = \frac{\ln \dfrac{A_{622}(z_1)}{A_{622}(z_2)}}{z_2 - z_1}, \quad (6)$$

where $A_{622}(z)$ was the absorbance of the actinometer solution at 622 nm after exposure at depth $z$. Most of the data were obtained between 2 and 4 attenuation lengths. (One attenuation length equals $1/K$) Within this depth range, the $K$ value was found to be constant within experimental error in all the suspensions. The table also includes approximate depths $z_{99}$ (equals $4.6/K$) at which 99% attenuation of surface radiation occurred in the suspensions. This depth is referred to as the photic zone in the balance of the paper.

High-speed centrifugation of portions of the suspensions employed in the above experiments yielded clear solutions that contained u.v.-absorbing dissolved substances. Thus, the $K$ value could be separated into two major components, equation (7):

$$K = K_D + K_s, \quad (7)$$

where $K_D$ is the component derived from dissolved substances and $K_s$ is the component from the suspended sediment. Assuming that $K_s$ is proportional to the concentration of suspended sediment $c_s$, specific attenuation coefficients $k_s$ (equals $K_s c_s^{-1}$) were computed for the sediments. In making these

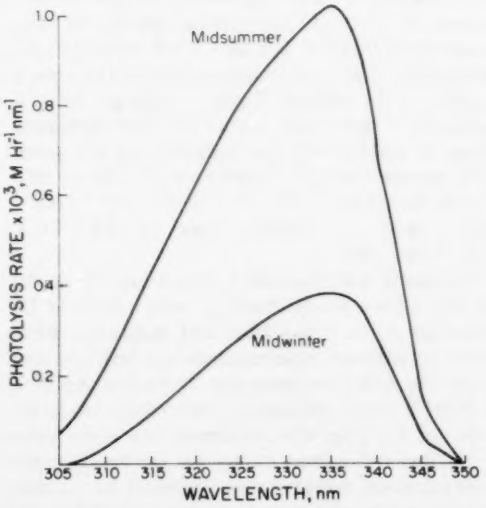


Fig. 1. Photolysis rate of the malachite green leucocyanide ($2.0 \times 10^{-3}$ M) actinometer as a function of wavelength; computed for midday, latitude 40°N.

Table 2. Attenuation coefficients for suspended sediments

| Sediment | Concentration (mg $l^{-1}$) | $K$, $cm^{-1}$* | 4.6/$k$, cm† | $(K\text{-}Da_{330})$ $cm^{-1}$‡ | $k_s$, 1 $mg^{-1}$ $cm^{-1}$§ |
|---|---|---|---|---|---|
| Oconee River | 82 ± 6 | 0.41 ± 0.01 | 11 | 0.35 | $4.8 \pm 0.5 \times 10^{-3}$ |
| USDA Pond | 17 ± 5 | 0.19 ± 0.01 | 24 | 0.14 | $8.2 \pm 3.0 \times 10^{-3}$ |
| Hickory Hill Pond | 44 ± 12 | 0.34 ± 0.02 | 13 | 0.34 | $7.7 \pm 2.5 \times 10^{-3}$ |
| Broad River | 41 ± 6 | 0.22 ± 0.02 | 20 | 0.16 | $4.0 \pm 0.9 \times 10^{-3}$ |
| Missouri River | 100 ± 20 | 0.35 ± 0.02 | 11 | 0.32 | $3.2 \pm 0.6 \times 10^{-3}$ |
| Mississippi River | 106 ± 3 | 0.53 ± 0.04 | 9 | 0.50 | $4.7 \pm 0.5 \times 10^{-3}$ |
| Humic acid (Fluka) | — | 0.25 ± 0.01 | 19 | 0.0 | — |

* Diffuse attenuation coefficient at greater than 2 attenuation lengths.
† Approximate depth at which 99% attentuation occurs.
‡ Component of $K$ due to light attenuation by suspended sediment.
§ Specific attenuation coefficient due to sediment; average value $5.4 \pm 2.0 \times 10^{-3}$ l $mg^{-1}$ $cm^{-1}$.

calculations, $K_D$ was subtracted from $K$ to obtain $K_s$. The value of $K_D$ was assumed to equal $Da_{330}$ where $D$ is the distribution coefficient obtained from experiments described later in the paper and $a_{330}$ is the beam attenuation coefficient of the supernatant derived from centrifugation of the suspensions. The latter was measured at 330 nm, the mean wavelength of sunlight absorbed by the actinometer. In further support of this wavelength selection, it was determined that the diffuse attenuation coefficient for a non-scattering solution of a commercial "humic acid" almost exactly equalled $Da_{330}$ for the solution (Table 2). The u.v. absorption spectrum of the humic acid solution was similar to spectra of the dissolved substances in the sediment suspensions.

The suspensions from the Oconee River, Broad River and USDA pond were obtained directly from the water column. In these water bodies, the sediment accounted for nearly all of the u.v. light attenuation (Table 2). The same was true of the other suspensions, which were resuspended bottom sediments. Specific attenuation coefficients for the suspended sediments were remarkably similar in view of the known variations in electronic absorption spectra of clay minerals (Karickhoff & Bailey, 1973). Moreover, the magnitude of $K_s$ was roughly related to the organic content of the sediment (Table 1), although the variations in $k_s$ and organic content were not sufficiently large to make a definitive judgment on this point. The specific attenuation coefficients for the six sediments ranged from $3.2 \times 10^{-3}$ to $8.2 \times 10^{-3}$ l $mg^{-1}$ $cm^{-1}$ with an average value of $5.4 \pm 2.0 \times 10^{-3}$ l $mg^{-1}$ $cm^{-1}$.

Assuming that $K$ equals $k_s c_s$, approximate depths of the 330 nm photic zone $z_{99}$ were calculated for locations on the Ohio River and Mississippi River (Fig. 2). Sediment concentrations ($c_s$) were obtained from the U.S. Environmental Protection Agency's STORET system. Because $k_s$ values were not available for the Ohio River sediments, the mean value of $k_s$ observed in these studies was employed for the computations. Average values computed for $z_{99}$ during the periods on the graph were 33 ± 31 cm for the Ohio River at Cincinnati and 7.7 ± 3.2 cm for the Mississippi River site. In comparison, the photic zone for clear ocean water at 330 nm is close to 50 m deep (Smith & Baker, 1979).

*Photolysis rates in sediment suspensions*

The photolysis rate (or conversion per unit time) of a pollutant in an infinitesimally small horizontal layer of a water body at depth $z$ and wavelength $\lambda$ is described by equation (8) (Zepp & Cline, 1977)

$$-\left(\frac{d[P]}{dt}\right)_{z,\lambda} = 2.303\phi\epsilon_\lambda I(z,\lambda)D[P]. \qquad (8)$$

In this equation, $\phi$ is the quantum yield for reaction, $\epsilon_\lambda$ is the molar absorptivity of the pollutant, $I(z, \lambda)$ is the radiant flux per unit area incident on the layer, $D$ is the distribution coefficient that was mentioned in the preceding section, and $[P]$ is the pollutant concentration. The distribution coefficient equals the mean pathlength of light in the layer divided by the thickness of the layer. The product $I(z), \lambda) \times D$ is referred to as scalar irradiance (Tyler & Preisendorfer, 1962). For photolysis rate computations, scalar irra-

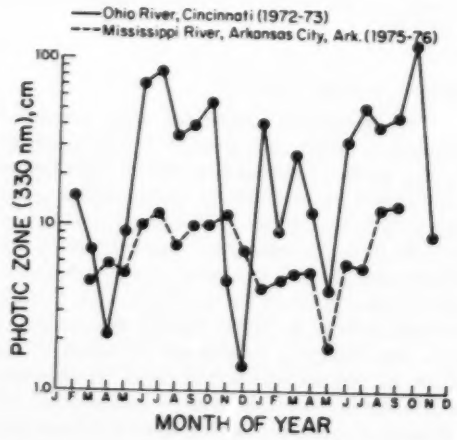
Ohio River, Cincinnati (1972-73)
Mississippi River, Arkansas City, Ark. (1975-76)
PHOTIC ZONE (330 nm), cm
100
10
1.0
J F M A M J J A S O N D J F M A M J J A S O N D
MONTH OF YEAR

Fig. 2. Computed penetration of solar u.v. radiation into the Ohio and Mississippi Rivers. Each data point corresponds to a sediment concentration measured at mid-month.

diance should be expressed as photons per unit area per unit time. The irradiance at depth $z$ can be expressed in terms of irradiance immediately below the surface of the water body, $W_\lambda$, by equation (9).

$$I(z, \lambda) = W_\lambda e^{-Kz}, \quad (9)$$

where $K$ is the diffuse attenuation coefficient at wavelength $\lambda$. Approximate values for $W_\lambda$ at sea level have been presented elsewhere (Zepp & Cline, 1977). In a river or other well-mixed water body, every molecule of pollutant in the water column is exposed to an equal amount of sunlight during a given period of time. Under these conditions, the radiation received by the pollutant is simply the space average of radiation in the water column $I_{a,\lambda}$, equation (10). (See Morowitz, 1950, for a similar derivation.)

$$I_{a,\lambda} = W_\lambda \frac{1 - e^{-Kz}}{Kz}. \quad (10)$$

The average photolysis rate $-(d[P]/dt)_{a,\lambda}$ is expressed by*:

$$-\left(\frac{d[P]}{dt}\right)_{a,\lambda} = 2.303\phi\epsilon_\lambda I_{a,\lambda} D[P]. \quad (11)$$

In most water bodies, the light is completely absorbed before it reaches the bottom, in which case $I_{a,\lambda}$ simply equals $W_\lambda (Kz)^{-1}$ where $z$ is the average depth.

Values of the distribution coefficient have been computed for water bodies in which scattering is unimportant compared to absorption (Whitney, 1941; Zepp & Cline, 1977). For middle u.v. radiation, $D$ typically equals or is less than 1.2. When scattering is important in a water body, computation of the distribution coefficient is much more difficult (Tyler & Preisendorfer, 1962). Scattering causes the radiation to become more diffuse as it moves down into the water, thus increasing the distribution coefficient. It was anticipated that this increase in $D$ would enhance photolysis rates within the photic zone, equation (11).

To document the effects of light scattering on photolysis rates, the photolysis of a phenyl ketone, γ-methoxy-*m*-trifluoromethylbutyrophenone (I) was studied in aqueous clay and sediment suspensions exposed to sunlight. The ketone absorbed exclusively in the middle u.v. region; its concentration ($4.0 \times 10^{-6}$ M) was kept sufficiently low that its light absorption made a negligible contribution to the attenuation coefficient of the suspensions. In all the suspensions and in distilled water, the ketone rapidly photoreacted under sunlight to form the expected photoproducts, *m*-trifluoroacetophenone and two isomeric cyclobutanols (Wagner *et al.*, 1972). The ketone was sufficiently hydrophilic that it did not sorb to the sediments or clays; the concentration of I in the water did not change when the suspended particles were removed by centrifugation.

The effect of scattering was first studied by comparing photolysis rate constants for I in water and in suspensions of u.v.-transparent clays, hectorite and halloysite, and the u.v.-absorbing clay, kaolinite (Karickhoff & Bailey, 1973) (Fig. 3). With both u.v.-transparent clays, the ratio of the rate constant in the suspension, $k_{clay}$, to that in the water, $k_{water}$, increased with increasing clay concentration. The increase is attributed to an increase in the distribution coefficient caused by forward scattering of the sunlight in the suspensions. In the case of kaolinite, the photolysis rate first increased with increasing clay concentration, then decreased as light attenuation began to offset the increase in the distribution coefficient caused by scattering.

These studies indicate that there is a considerable difference in the scattering efficiencies of the minerals. The differences possibly can be attributed to dissimilarities in particle size. It is also of interest that the maximum value of 1.8 for $k_{clay}/k_{water}$ in the halloysite suspensions is close to that expected for a non-absorbing suspension in which the light is completely diffuse. Finally, these results suggest that the enhanced photolysis rates of polycyclic aromatic hydrocarbons observed by McGinnes (1974) in kaolinite suspensions are probably mainly attributable to light scattering and not to enhanced photoreactivity on the clay surface.

Photolysis rates of I were also determined under sunlight in the same natural sediment suspensions that were used in determinations of the diffuse attenuation coefficients (Table 2). Stirred solutions of I ($4 \times 10^{-6}$ M) in the sediment suspensions and in distilled water were simultaneously exposed to sunlight, and first-order rate constants were computed

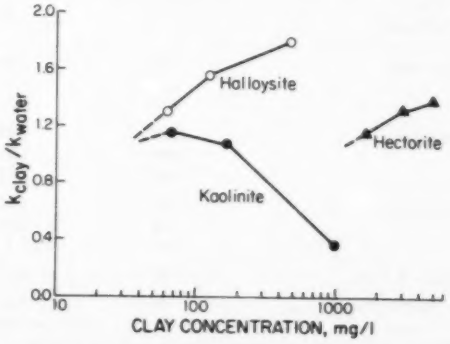


Fig. 3. Effects of suspended clays upon the photolysis of (I); $k_{clay}$ and $k_{water}$ are first-order rate constants for photolysis in clay suspensions and in distilled water, respectively at a depth of 2.9 cm under sunlight.

* Zepp & Cline (1977) previously derived the following equation that describes photolysis rates in a homogeneous medium.

$$-\left(\frac{d[P]}{dt}\right)_{a,\lambda} = \frac{W_\lambda(1 - 10^{-\alpha_\lambda l})\phi\epsilon_\lambda}{\alpha_\lambda z}[P].$$

It can be shown that this equation is a special case of equation (12) in which $K = 2.303 D\alpha_\lambda$ and pathlength $l = Dz$.

Table 3. Scattering effects of some suspended sediments

| Sediment | Sediment concentration ($mg\,l^{-1}$) | Depth, cm | $min^{-1} \times 10^3$ $k_s$* | $k_{water}$† | $D/D_w$ | Average distribution coefficient ($D$) |
|---|---|---|---|---|---|---|
| Oconee River | 82 | 9.4 | 6.6 | 19.7 | 1.33 | 1.6 |
| USDA Pond | 17 | 8.3 | 10.8 | 17.9 | 1.18 | 1.4 |
| Hickory Hill Pond | 44 | 9.7 | 6.3 | 12.9 | 1.69 | 2.0 |
| Broad River | 41 | 9.7 | 6.4 | 14.7 | 1.06 | 1.3 |
| Missouri River | 100 | 9.2 | 7.6 | 18.2 | 1.40 | 1.7 |
| Mississippi River | 105 | 9.6 | 3.0 | 12.4 | 1.23 | 1.5 |
| Humic acid (Fluka) | — | 9.7 | 5.9 | 15.0 | 1.03 | 1.2 |

* First-order rate constant for photolysis of (I) in the sediment suspension exposed to sunlight at midday.
† Rate constant for photolysis of (I) in distilled water solution that was exposed to sunlight at the same time as the suspension.

for the decrease in concentration of I with time. Because sunlight is not significantly attenuated in distilled water at the depth employed (9.6 cm), the ratio of the photolysis rate constant in the sediment suspensions $k_s$ to that in distilled water $k_{water}$ can be expressed as [see equations (10) and (11)]:

$$\frac{k_s}{k_{water}} = \left(\frac{1 - e^{-Kz}}{Kz}\right)\frac{D}{D_w},$$

where $D$ and $D_w$ are average distribution coefficients in suspension and distilled water, respectively. Employing this equation, the photolysis rate data, and the diffuse attenuation coefficients in Table 2, the ratio $D/D_w$ was computed for the suspensions (Table 3). As a test of this procedure, $D/D_w$ was also computed for a non-scattering solution of a commercial humic acid that had about the same diffuse attenuation coefficient as the suspensions (Table 2). In this solution, the computed value of $D/D_w$ corresponded closely to the expected value of unity for a non-scattering medium. With most of the suspensions, scattering caused enhancements of the distribution coefficient. Assuming that the distribution coefficient in distilled water was about 1.2 (Zepp & Cline, 1977), values were computed for $D$ (Table 3). The mean value of $D$ was $1.6 \pm 0.2$ for the six suspensions. Thus, on the average, the mean photolysis rate of (I) within the photic zone was about 30% larger in the suspensions than in clear water.

Earlier in the paper it was pointed out that the penetration of sunlight into a water body can be underestimated if beam rather than diffuse attenuation coefficients are used to assess light transmittance, see equations (4 and 5). This is particularly true in water bodies containing high concentrations of suspended sediments. Table 4 illustrates the gross errors that can result when beam attenuation coefficients are employed in the computation of photolysis rates in clay or sediment suspensions. Photolysis rate constants, $k_{calc}$, were calculated by computer as described by Zepp & Cline (1977). Beam attenuation coefficients for the suspensions of sediments from the Oconee and Mississippi River (Table 4) were over three times larger than the diffuse attenuation coefficients (Table 2). It is apparent that a large fraction of the beam attenuation by the suspensions of halloysite, hectorite, and kaolinite is the result of forward scat-

Table 4. Comparison of observed photolysis rate constants for (I) in clay or sediment suspensions with rate constants computed assuming that beam attenuation by the suspensions is entirely the result of absorption

| Clay or sediment | Concentration ($mg\,l^{-1}$) | $a_{330}$, $cm^{-1}$ | $min^{-1} \times 10^3$ $k_{water}$* | $k_{calc}$† | $k_{obs}$‡ | $k_{obs}/k_{calc}$ |
|---|---|---|---|---|---|---|
| Halloysite§ | 62 | 1.06 | 20 | 5.3 | 26 | 4.9 |
| | 124 | 2.11 | 20 | 2.7 | 31 | 11 |
| | 459 | 6.86 | 20 | 0.84 | 36 | 43 |
| Hectorite§ | 1630 | 0.932 | 13 | 3.8 | 15 | 3.9 |
| | 2860 | 1.52 | 13 | 2.4 | 17 | 7.1 |
| | 4900 | 3.12 | 13 | 1.2 | 18 | 15 |
| Kaolinite§ | 66 | 1.12 | 13 | 3.3 | 15 | 4.5 |
| | 166 | 2.69 | 13 | 1.4 | 14 | 10 |
| | 997 | 16.4 | 13 | 0.23 | 4.8 | 21 |
| Oconee River¶ | 82 | 1.36 | 20 | 1.5 | 6.6 | 4.3 |
| Mississippi River¶ | 105 | 1.76 | 12 | 0.73 | 3.0 | 4.1 |

* Rate constant for photolysis of (I) in distilled water
† Computed assuming that beam attenuation is totally attributable to light absorption, i.e., assuming that $K = D_w a$.
‡ Rate constant for photolysis of (I) in clay or sediment suspension.
§ Depth of 2.9 cm.
¶ Depth of 9.6 cm.

tering. The difference in computed and observed rates increases with increasing clay concentration.

## CONCLUSIONS

These studies indicate that light attenuation by suspended sediments is likely to be one of the most important determinants of the photolysis rates of pollutants in many inland water bodies. Direct measurements of solar u.v. radiation (280–340 nm) in suspensions of natural sediments at concentrations of 17–106 $mg^{-1}$ indicate that greater than 99% of the incident radiation is attenuated in the top 25 cm. The suspended sediments were almost completely responsible for the light attenuation in three Georgia water bodies. Specific diffuse attenuation coefficients for sediments from water bodies in Georgia, Mississippi, and Montana fell in a surprisingly narrow range.

Large underestimates of photolysis rates resulted when beam attenuation coefficients, $\alpha$, were employed to compute the effects of light attenuation on photolysis in clay and sediment suspensions. The underestimates were attributable to the fact that forward scattering is an important mode of beam attenuation in the suspensions; forward scattered light is not lost but remains available for photolysis. Moreover, it was demonstrated that photolysis rates are enhanced by the increased diffuseness of light caused by scattering in the suspensions. Thus, average photolysis rates within the photic zone are generally larger in turbid than in clear water bodies. This scattering effect was responsible for rate enhancements of a factor of up to 1.8 in clay suspensions, but somewhat smaller enhancements were observed in suspensions of natural sediments. In view of the complexity of the effects of scattering, it obviously would be best to employ diffuse attenuation coefficients to estimate effects of light attenuation in turbid water bodies. An equation [equation (12)] that employs $K$ values to compute photolysis rates was presented in this paper.

Finally, it should be emphasized that the attenuation coefficients presented here are based on broadband light measurements that apply only approximately to 330-nm u.v. light. These studies should be followed up by narrow-band measurements that will precisely define the $K$-values as a function of wavelength.

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